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			19b. TELEPHONE NUMBER (include area code) (321) 638-1436	

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## Quarterly Progress Report

**Project Title:** Simultaneous Extraction of Lithium and Hydrogen from Seawater

**Project Period:** 7/26/2010 – 7/25/2011

**Reporting Period:** July 26, 2010 – October 25, 2010

**Date of Report:** October 26, 2010

**Recipient:** University of Central Florida

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**Contact:** Pyoungcho Choi, UCF, 321 638-1436, [pchoi@fsec.ucf.edu](mailto:pchoi@fsec.ucf.edu)

**Program Officer:** Dr. Michele Anderson, ONR Code: 332, [michele.anderson1@navy.mil](mailto:michele.anderson1@navy.mil)

**Project Objective:** The ultimate goal of the proposed research is to demonstrate a novel electrolytic process for extracting Li from seawater, which contains a number of valuable metals (Table1).<sup>1</sup> The technical objectives of this research are to construct an electrolytic cell, develop high capacity lithium ion adsorbing materials, design solid electrolytes conducting Li ion subject to concentration and potential gradients, and evaluate the process energy consumption and Li production costs.

Table 1. Concentrations and amount of dissolved metals ions in the sea, compared with the estimated land reserves.

Element	Concentration (ppm)	Total Oceanic Abundance (tons)	Mineral Reserves in Land (tons)
Na	10,800	$1.40 \times 10^{16}$	-
Mg	1,290	$1.68 \times 10^{15}$	$2.20 \times 10^9$
Ca	411	$5.34 \times 10^{14}$	-
K	392	$5.10 \times 10^{14}$	$8.30 \times 10^8$
<b>Li</b>	<b>0.1780</b>	<b><math>2.31 \times 10^{11}</math></b>	<b><math>4.10 \times 10^6</math></b>
Ba	0.0210	$2.73 \times 10^{10}$	$1.90 \times 10^8$
Mo	0.0100	$1.30 \times 10^{10}$	$8.60 \times 10^6$
Ni	0.0066	$8.58 \times 10^9$	$6.70 \times 10^7$
Zn	0.0050	$6.50 \times 10^9$	$1.80 \times 10^8$
Fe	0.0340	$4.42 \times 10^9$	$1.50 \times 10^{11}$
U	0.0330	$4.29 \times 10^9$	$2.60 \times 10^6$ - $5.47 \times 10^6$
V	0.0190	$2.47 \times 10^9$	$1.30 \times 10^7$

**Approach:** Figure 1 shows the schematic of lithium extraction from seawater by an electrochemical process.  $\text{Li}^+$  ion containing seawater is introduced in the anode in which seawater is dissociated to oxygen, protons and electrons, while a lithium extracting solution is fed to the cathode side of the cell. A thin and highly ion-conductive electrolyte is placed between the electrodes. The migration of  $\text{Li}^+$  depends on the potential applied between the anode and

cathode. At low potential, i.e.,  $<1.23\text{V}$ ,  $\text{Li}^+$  ion may migrate to the negative electrode without the water dissociation reactions. At high potential, i.e.,  $>1.23\text{V}$ ,  $\text{Li}^+$  ions in seawater are forced to diffuse through the electrolyte to the negative side where they combine with hydroxyl ions ( $\text{OH}^-$ ), co-producing  $\text{H}_2$  and  $\text{Li}$  solution from seawater. As the anode, carbon felt or water splitting electrocatalysts will be used.  $\text{Li}$ -adsorbing materials, e.g.,  $\text{LiMn}_2\text{O}_4$ , will be prepared and coated onto the anode to increase the  $\text{Li}^+$  ion adsorption, and subsequent diffusion to the cathode through electrolytes. As the electrolyte, polymer (e.g., Nafion) and  $\text{Li}^+$  ion selective LISICON (lithium super ionic conductor) will also be implemented and their role in the transport of  $\text{Li}^+$  ions from the anode to the cathode side will be quantitatively analyzed.

An electrolytic cell will be designed and various electrochemical reaction & process parameters will be determined. An overall performance equation will be developed to describe the relation among the potential, current and concentration of  $\text{Li}^+$  ions in the anolyte and catholyte. The process will be optimized and a basic cost analysis of the process will be performed.

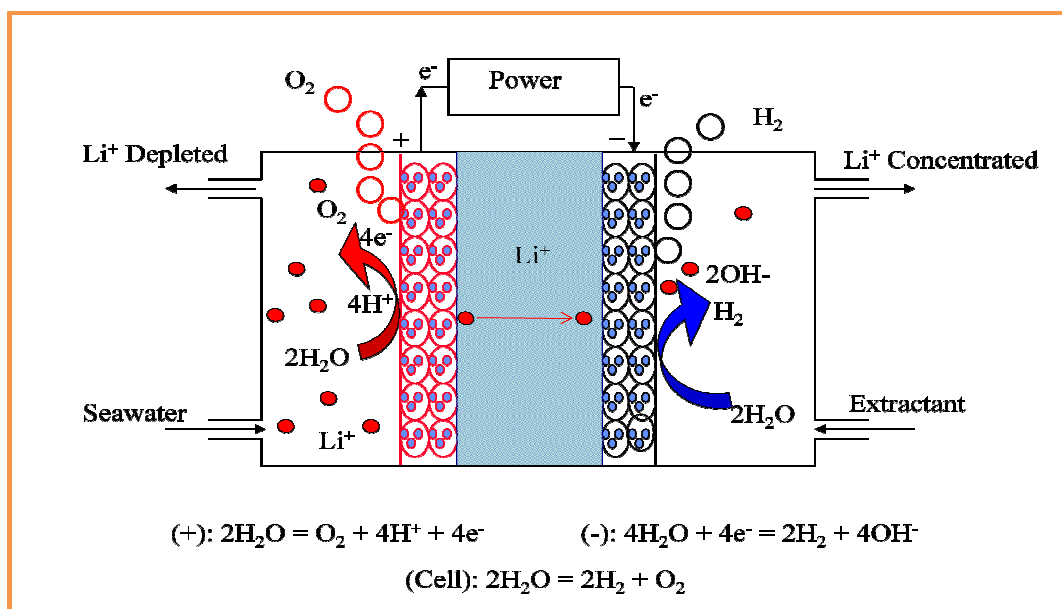


Figure 1. Schematic of the electrochemical process extracting lithium from seawater

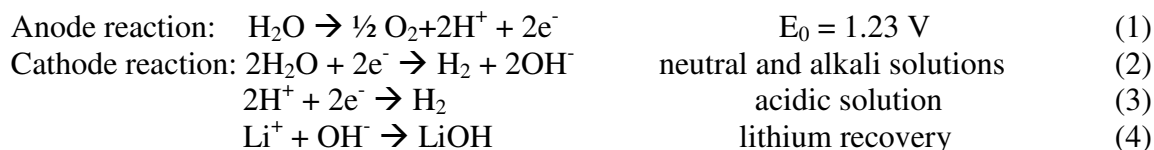


Figure 2 shows structure of  $\text{LiMn}_2\text{O}_4$  materials.<sup>2</sup> Lithium atom is in an 8a tetrahedral site in the spinel structure. Acid treatment of the  $\text{LiMn}_2\text{O}_4$  removes lithium and generates atomic holes, which allow lithium ion to access the site, but not other ions. The mechanism of  $\text{Li}$  insertion/extraction has been extensively studied.<sup>3-5</sup>



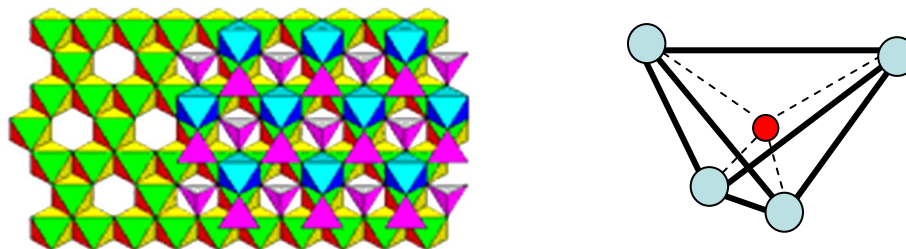
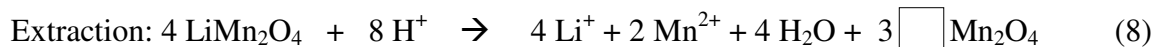
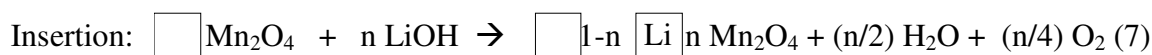
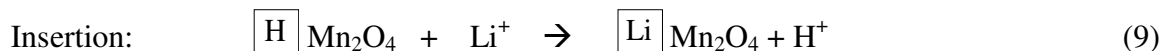


Figure 2. An example of lithium adsorbent, LiMn<sub>2</sub>O<sub>4</sub> (Li in 8a tetrahedral site).

For LiMn<sub>2</sub>O<sub>4</sub>, it proceeds by a redox mechanism which generates oxygen in the insertion as follows:



whereas for Li<sub>1.33</sub>Mn<sub>1.67</sub>O<sub>4</sub> and Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, it proceeds mostly by ion-exchange mechanism as



where  $\square$  represents a tetrahedral vacant site and n is the number of moles of inserted Li. The manganese oxide adsorbents are very efficient and other ions in seawater do not interfere with Li for the adsorption.

**Project Status:** A Li<sup>+</sup> adsorbing material was synthesized using a solid-state reaction and Li<sup>+</sup> conducting ceramic materials, namely LISICON, were also prepared by a solid-state reaction. As an initial experiment, carbon felt which does not have catalytic activity for water splitting, was used as the anode and cathode. An electrochemical cell was constructed and tested with the materials incorporated. Electrochemical potential was applied between the anode and cathode, and current-potential curves are obtained. A number of electrodes, adsorbents and electrolytes are being prepared, characterized, and tested in the electrolytic cell.

Synthesis of Li<sup>+</sup> adsorbents: LiMg<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> was prepared by solid state reaction. Li<sub>2</sub>CO<sub>3</sub>, Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and MnCO<sub>3</sub> were mixed at a 1:0.5:1.5 molar ratio with ball mill machine for 30 min, and calcined at 600°C for 4 hours. Surface area and porosity were analyzed by BET.

Synthesis of LISICON: The 80Li<sub>2</sub>S:20P<sub>2</sub>S<sub>5</sub> glassy powders were prepared from the mixture of Li<sub>2</sub>S and P<sub>2</sub>S<sub>5</sub> crystalline powders.<sup>6</sup> The mixture was mechanically milled. The powders were heated to 230°C and kept at the temperature for 4 hours, and slowly cooled down. A commercially available LISICON film (Ohara, 25.4mm x 25.4mm x 1mm) was also used as an initial experiment.

Construction of Electrolytic Cell: An electrolytic cell was made by incorporating the cell components with a two-pump flow system.

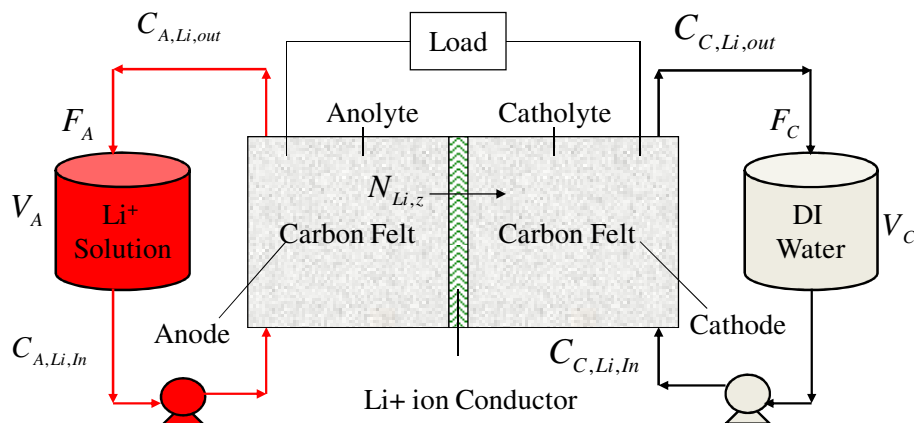


Figure 1 Schematic of electrolytic cell extracting  $\text{Li}^+$  ion from seawater or Li-concentrates.

Quantification of  $\text{Li}^+$  ion Concentration in Solution: The concentration of  $\text{Li}^+$  ion in solution was analyzed by Ion Chromatography.  $\text{LiNO}_3$  solution was used to obtain a calibration curve.

## Results

### BET and porosity of the prepared adsorbents

The specific surface area and pore volume of the prepared sieve1 adsorbent are shown in Table 1. The molecular formula of the sieve1 composed of Li, Mg and Mn are being measured by AAS (Atomic Adsorption Spectroscopy). Also atomic structure and grain size of the adsorbent is being investigated by XRD.

	BET Surface Area, $\text{m}^2/\text{g}$	Pore volume $\text{cc/g}$
sieve 1	8.997	0.0375

### $\text{Li}^+$ ion calibration by Ion Chromatography

The concentration of  $\text{Li}^+$  ion in solution was determined by IC. Figures 2 and 3 show an IC chromatogram of 1 ppm and a calibration curve of  $\text{Li}^+$  ions from 0.1ppm to 1ppm, respectively.

### Operating Conditions:

- Effluent: 20 mM Methanesulfonic acid, Effluent flow rate=1.0ml/min
- Detection: Suppressed Conductivity
- Suppressor: Cation Self-Regenerating Suppressor (CSRS ULTRA II, 4mm)  
AutoSuppression Recycle Mode
- Applied Current: 59 mA
- Injection volume: 25 microliter

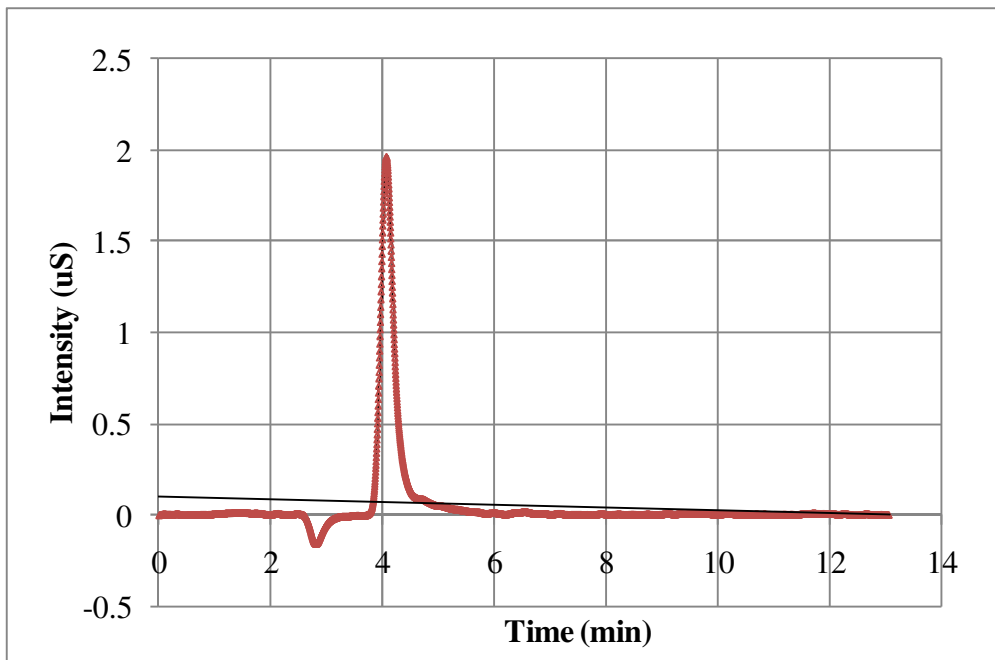


Figure 2. IC chromatogram of 1 ppm  $\text{Li}^+$  ion solution

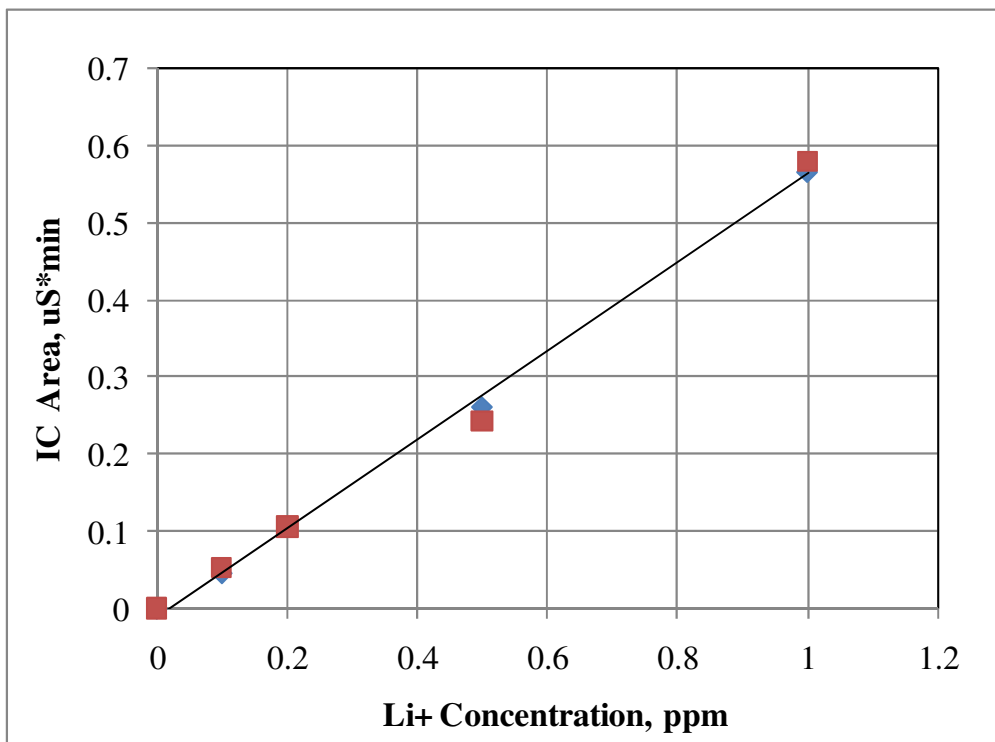


Figure 3. Calibration curve of  $\text{Li}^+$  ions from 0.1ppm to 1ppm.

### Linear Sweep Voltammetry 1

First, linear sweep voltammetry (LSV) experiment was carried out. The anolyte was 1ppm  $\text{Li}^+$  ion solution and catholyte was deionized water. The potential range of 0-3V was scanned and resulting current was obtained. No precious electrode was used and Nafion was used as the electrolyte.

#### Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: 1ppm  $\text{Li}^+$  ion solution of 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte Flow rate: 10ml/min

Electrolyte: Nafion

Figure 4 shows the LSV of the electrolytic cell with the operating conditions above. According to the chromatogram, more than 2V is required to generate current density of  $1 \text{ mA/cm}^2$ . No gas evolution was observed due to the absence of electrocatalysts for the electrochemical water splitting reactions.

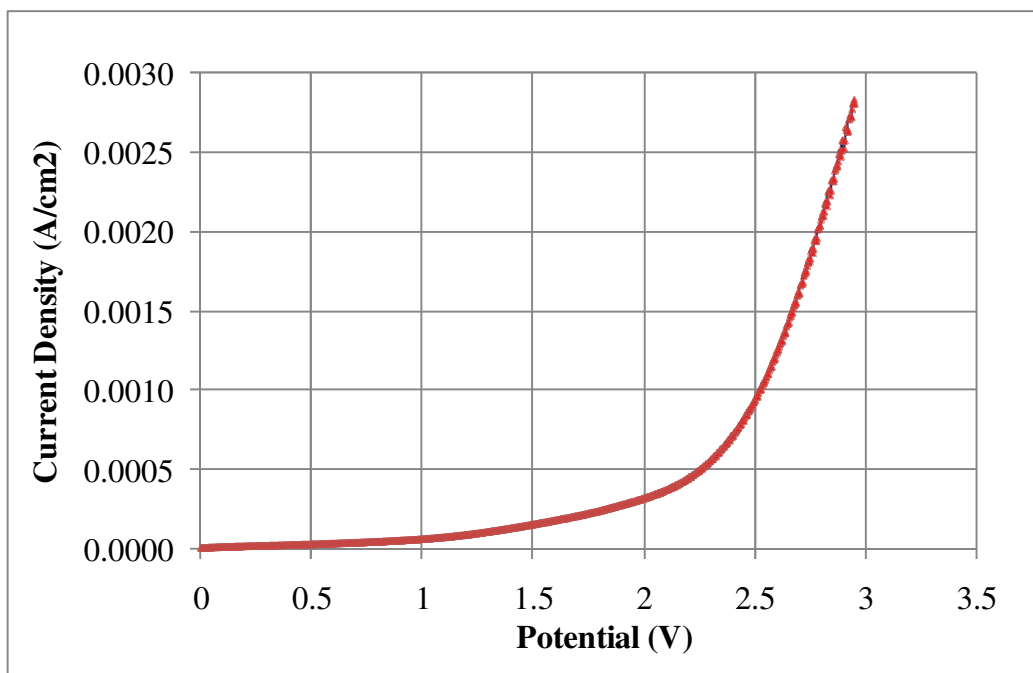


Figure 4. Linear sweep voltammogram of the electrolytic cell.

### Galvanostatic Experiment 1

The electrolytic cell current was set at  $1 \text{ mA/cm}^2$  and resulting voltage was recorded with time. Anolyte as well as catholyte from the cell was collected every thirty minutes for the analysis of  $\text{Li}^+$  ion concentration. As shown in Figure 5, the cell was stable and potential was decreased over time.

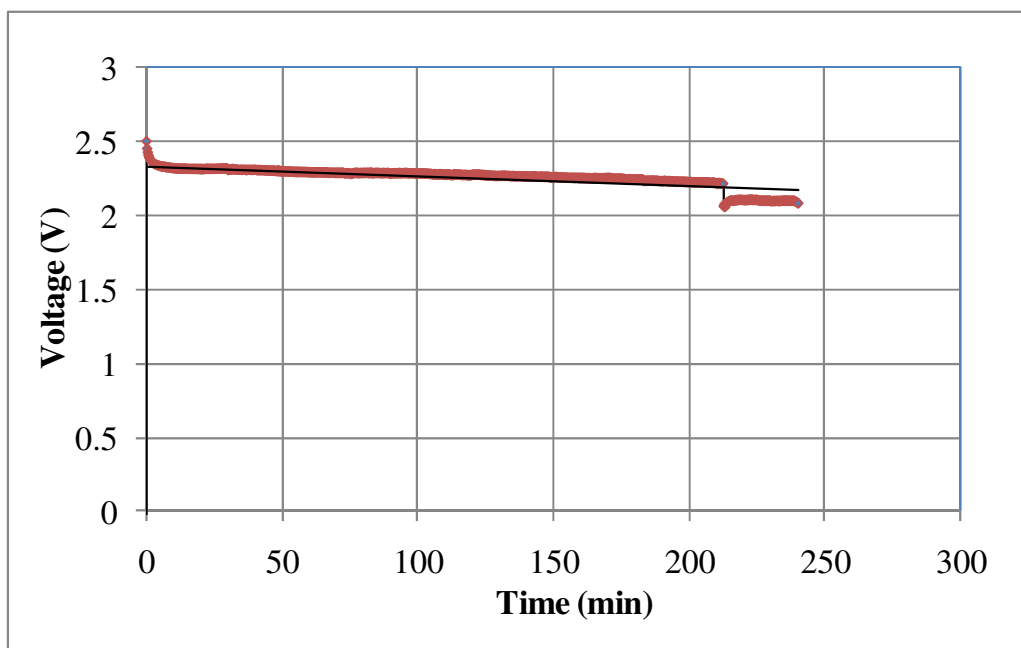


Figure 5. Galvanostatic voltammogram of the electrolytic cell.

The concentration of  $\text{Li}^+$  ions in the anolyte and catholyte was determined by IC and shown in Figure 6. The concentration of anolyte decreases because of the diffusion of  $\text{Li}^+$  ions to the catholyte under the electrode potential. The diffusion is also assisted by the chemical potential difference, i.e., concentration gradient, across the membrane. The concentration of catholyte was increased with time and higher than that of anolyte due to the lower working volume of the solution. After 2 hours of operation, the concentration of  $\text{Li}^+$  ion in the catholyte was 0.76 ppm, while that in anolyte was 0.68 ppm. Thus, the  $\text{Li}^+$  ion can be concentrated by the electrolytic cell by employing small volume of catholyte reservoir.



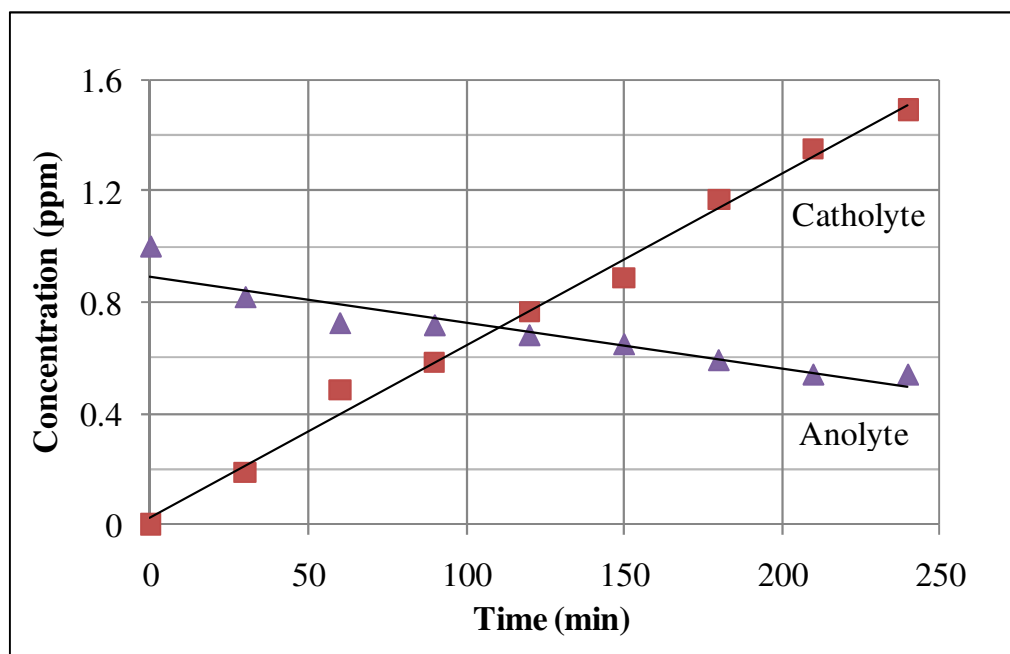


Figure 6.  $\text{Li}^+$  ion concentration in the anolyte and catholyte with time.

### Linear Sweep Voltammetry 2

LSV experiment employing a lithium superionic conductor (LISICON) was carried out using the  $\text{Li}^+$  ion solution. The potential range of 0-3V was scanned and resulting current was obtained.

#### Operating Conditions:

Anode: carbon felt (0.5mm)

Anolyte: 1ppm  $\text{Li}^+$  ion solution of 300ml

Anolyte flow rate: 10ml/min

Cathode: carbon felt (0.5mm)

Catholyte: DI water of 100ml

Catholyte flow rate: 10ml/min

Electrolyte: LISICON (Ohara Inc.)

Figure 7 shows the LSV of the electrolytic cell. The current is relatively low, compared to that of the Nafion membrane. The current density of  $0.1\text{mA}/\text{cm}^2$  could be obtained at 1.7V. No gas evolution was observed by the electrochemical water splitting reactions. Figure 8 shows the concentration of catholyte when a galvanostatic experiment was carried out at  $0.1\text{mA}/\text{cm}^2$ . The  $\text{Li}^+$  ion concentration in the catholyte increases to 0.05 ppm after 2 hours of operation.

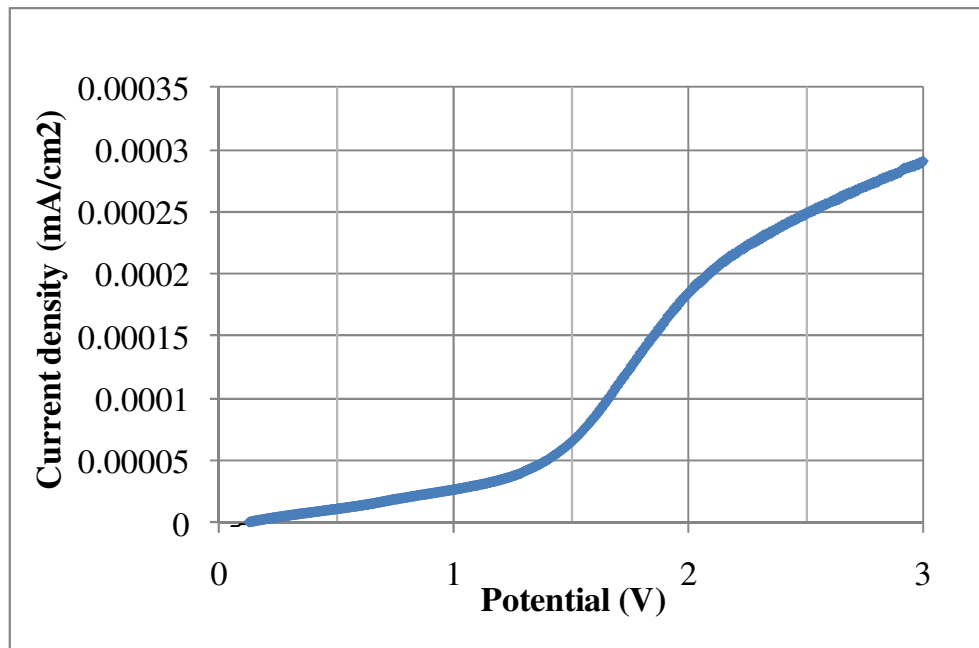


Figure 7. Linear sweep voltammogram of the electrolytic cell.

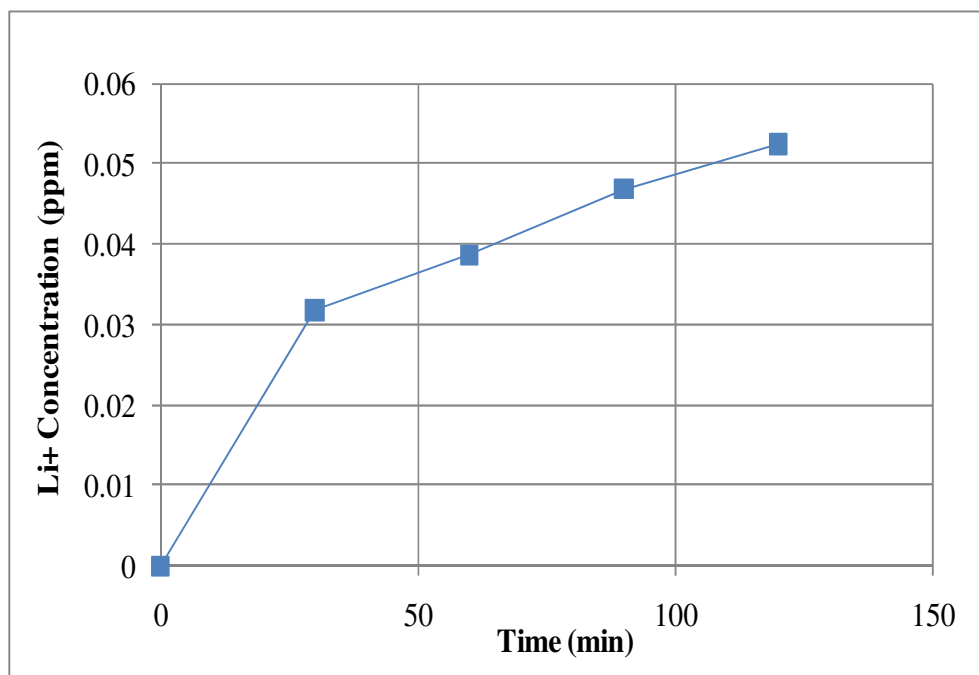


Figure 8. Li<sup>+</sup> ion concentration in the catholyte with time.

## Analysis

A simple analysis is being performed to understand the role of the electrocatalysts,  $\text{Li}^+$  adsorbents and conductors in the electrolytic cell.

The basic conservation equations are developed.

### *Anolyte Reservoir*

$$V_A \cdot \frac{dC_{A, \text{Li}}}{dt} = F_A C_{A, \text{Li}, \text{In}} - F_A C_{A, \text{Li}, \text{out}}$$

where  $V_A$  is the volume of anode reservoir (seawater tank),  $F_A$  is the volumetric flow rate of the working fluid in the anode,  $C_{A, \text{Li}, \text{In}}$  and  $C_{A, \text{Li}, \text{out}}$  are the concentration of  $\text{Li}^+$  ion in the anode side entering and exiting the electrolytic cell, respectively,

### *Anode Side of Electrolytic Cell*

$$F_A C_{A, \text{Li}, \text{In}} - F_A C_{A, \text{Li}, \text{out}} = N_{\text{Li}, z} \cdot A_M$$

$N_{\text{Li}, z}$  is the flux of i in z-direction (across the membrane), and  $A_M$  ( $\text{cm}^2$ ) is the geometric area of the MEA.

### *Electrode Layer*

$$\frac{dN_{\text{Li}, z}}{dz} = r_A$$

where  $r_A$  is the rate per volume of electrode layer

### *$\text{Li}^+$ Conducting Electrolyte*

If constant chemical potential throughout the electrolyte is assumed,

$$i = -\sigma \frac{d\phi^\alpha}{dz}$$

where  $\sigma$  is the conductivity of the electrolyte and  $\phi^\alpha$  is the potential at the electrolyte phase  $\alpha$ .

### *Cathode Side of Electrolytic Cell*

$$F_C C_{C, \text{Li}, \text{In}} - F_C C_{C, \text{Li}, \text{out}} = N_{\text{Li}, z} \cdot A_M$$

### *Catholyte Reservoir*

$$V_C \cdot \frac{dC_{CC,Li}}{dt} = F_C C_{C,Li,in} - F_A C_{C,Li,out}$$

A performance equation will be generated and the effect of the adsorbent, Li<sup>+</sup> ion conductor and electrocatalyst on the performance of the Li<sup>+</sup> ion extraction will be quantitatively analyzed.

### Plans for Next Quarter:

The planned activities for next quarter include:

- Characterize the prepared adsorbents and glass-ceramic electrolytes
- Prepare electrodes and thin films of Li<sup>+</sup> ion selective electrolytes
- Incorporate the adsorbents and Li<sup>+</sup> ion conductor in the electrolytic cell
- Use seawater as the working catholyte solution and characterize the materials and cell
- Optimize the electrochemical Li extraction process (examine the electrochemical cell variables including cell potential, amount of adsorbent, thickness of solid electrolyte, and flow rate of seawater through the cell, etc.)

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